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INTENSITY FORMULAS FOR TRIPLET BANDS

A. Budo

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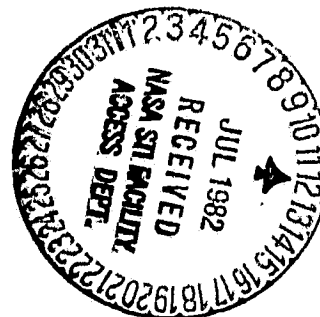
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16. Abstract This article is a study of intensity formulas for triplet bands. The author refers to previous works in this area and presents the mathematics involved in determining the quantitative intensity measurements in triplet bands. 3 Tables, 2 Figures, 9 Equations and 6 References are contained in the 10 pages.			
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A. Budo**

Explicit expressions for the intensity distribution in the branches of $^1\Sigma \leftrightarrow ^1\Pi$ and $^1\Sigma \leftrightarrow ^3\Pi$ bands are given, which ought to be valid for all values of the coupling constant Y of the $^3\Pi$ terms. The corresponding formulas can also be derived for the $^3\Pi \rightarrow ^3\Pi$ bands. The intensity distribution calculated according to the formulas given is compared with measurements of PH, $^3\Pi \rightarrow ^1\Sigma$ bands. There is quite good quantitative agreement.

The problem of the intensity distribution in the multiplet band branches of the two atomic molecule was treated by Hill and van Vleck, to the extent that they dealt with terms among the Hund cases a--b. This is almost always the case, and in principle, this problem was solved. They gave the elements of the amplitude matrix q_a [1] and of the energy matrix H_a [2], so that based on the equation

$$SH_a\tilde{S}^* = W \quad (1)$$

the energy values W and the transformation matrix S can be calculated. Then according to

$$q' = Sq_a\tilde{S}^* \quad (2)$$

($S\tilde{S}^* = 1$) it is possible to calculate the amplitudes q_{ik} . For doublet bands, it was possible to give explicit expressions for the intensity distribution, and this was compared with experience [3]. The difficulty for triplet bands is caused by the fact that we do not have any simple expression for the $^3\Pi$ energies, which for all values of the coupling constant $Y = A/B$ are valid with precision accuracy. The expressions derived by the author [4] are not suitable for this purpose. Therefore, we select the following energy expression

* Numbers in margin indicate pagination of foreign text

** Communication from the Physical Institute of the Royal Hungarian University for Technical and Economic Sciences (recd. March 11, 1937)

$$\left. \begin{aligned} \frac{W_1}{B} &= -1 + J(J+1) - [Y(Y-4) + 4J^2]^{1/2}, \quad \frac{W_2}{B} = -1 + J(J+1), \\ \frac{W_3}{B} &= -1 + J(J+1) + [Y(Y-4) + 4(J+1)^2]^{1/2}. \end{aligned} \right\} \quad (3)$$

These are sufficiently accurate and for $Y = 0$ and $Y = \pm \infty$ respectively, they turn into the exact formulas in cases b and a respectively (in the case of W_2 in case a, up to an additional constant 2 which is inconsequential here).

From these values and the known expression for H_a , based on Equation (1), it is possible to calculate the elements of the transformation matrix $S(^3//)$, and in a similar way, the elements of $S(^3\Sigma)$. Then according to (2), we can also calculate the elements of

$q(^3\Sigma \leftrightarrow ^3//)$, the squares $|q_i|^2$ of which are decisive (the so-called i-factors) for the intensity distribution in the $^3\Sigma \leftrightarrow ^3//$ branches. The final expressions in all 27 branches are shown in Table 1. Here and in the following we have

$$u_1 = [Y(Y-4) + 4J^2]^{1/2}, \quad u_2 = [Y(Y-4) - 4(J+1)^2]^{1/2} \quad (4)$$

and

$$\left. \begin{aligned} C_1(J) &= J(J+1) Y(Y-4) + 2(2J+1)(J-1)J(J+1), \\ C_2(J) &= Y(Y-4) + 4J(J+1), \\ C_3(J) &= (J-1)(J+2) Y(Y-4) + 2(2J+1)J(J+1)(J+2) \end{aligned} \right\} \quad (5)$$

for normal terms (Y positive). For the reverse terms, on the other hand, (Y negative), the coefficient of $Y(Y-4)$ in $C_1(J)$ equals $(J-1)(J+2)$ instead of $J(J+1)$. In $C_3(J)$, it is equal to $J(J+1)$ instead of $(J-1)(J+2)$ *. The formulas are valid for all values of Y and as special cases, they contain the formulas for

$^3\Sigma \leftrightarrow ^3// (b)$, $^3\Sigma \leftrightarrow ^3//_{\text{norm}} (a)$, $^3\Sigma \leftrightarrow ^3//_{\text{inv}} (a)$, that is, respectively $Y = 0, +\infty, -\infty$.

*The exact expressions for $C_1(J)$ is $C_1(J) = J(J+1) Y(Y-4) + 2(2J+1)(J-1)J(J+1) - (Y-2)[Y(Y-4) + 4J^2]^{1/2} - Y(Y-4) + 4J$.

but the simplification given in the text is permissible. A similar statement applies for $C_3(J)$.

TABLE 1.

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${}^{\mu}\Sigma \rightarrow {}^{\mu}\mu$	${}^{\mu}\mu \rightarrow {}^{\mu}\Sigma$	1-factors
$P_1(J)$	$R_1(J-1)$	$\frac{(J^2-1)[(J+1)u_1-Y+2J^2]^2}{(2J-1)C_1(J)}$
$Q_1(J)$	$Q_1(J)$	$\frac{[(J^2+J-1)u_1+(Y-2)+2J(J^2-1)]^2}{J C_1(J)}$
$R_1(J)$	$P_1(J+1)$	$\frac{J[J(J+2)u_1+(J+2)(Y-2)+2(J-1)(J+1)^2]}{(J+1)(2J+3)C_1(J)}$
${}^qP_{11}(J)$	${}^qR_{11}(J-1)$	$\frac{(J^2-1)[(J+1)(Y-2)-u_1]^2}{J C_1(J)}$
${}^sQ_{11}(J)$	${}^sQ_{11}(J)$	$\frac{(2J+1)[(J^2+J-1)(Y-2)+u_1]^2}{J(J+1)C_1(J)}$
${}^sR_{11}(J)$	${}^oP_{11}(J+1)$	$\frac{J(J+2)[J(Y-2)+u_1]^2}{(J+1)C_1(J)}$
${}^sP_{11}(J)$	${}^sR_{11}(J-1)$	$\frac{(J-1)^2(J+1)[(J+1)u_1-(Y-2)-2J(J+1)]^2}{J(2J-1)C_1(J)}$
${}^sQ_{11}(J)$	${}^oQ_{11}(J)$	$\frac{[(J^2+J-1)u_1+(Y-2)-2(J-1)(J+1)^2]^2}{(J+1)C_1(J)}$
${}^tR_{11}(J)$	${}^N P_{11}(J+1)$	$\frac{J(J+2)[J u_1+Y-2J^2]^2}{(2J+3)C_1(J)}$
${}^oP_{11}(J)$	${}^sR_{11}(J-1)$	$\frac{2(J^2-1)Y^2}{(2J-1)C_2(J)}$
${}^sQ_{11}(J)$	${}^sQ_{11}(J)$	$\frac{2[J(Y-2)-2]^2}{J C_2(J)}$
${}^qR_{11}(J)$	${}^qP_{11}(J+1)$	$\frac{2J[(J+1)Y-2(2J+3)]^2}{(J+1)(2J+3)C_2(J)}$
$P_2(J)$	$R_2(J-1)$	$\frac{8(J-1)(J+1)^2}{J C_2(J)}$
$Q_2(J)$	$Q_2(J)$	$\frac{8(2J+1)(J^2+J-1)^2}{J(J+1)C_2(J)}$
$R_2(J)$	$P_2(J+1)$	$\frac{8J^2(J+2)}{(J+1)C_2(J)}$
${}^qP_{22}(J)$	${}^qR_{22}(J-1)$	$\frac{2(J+1)[J(Y-4)+2]^2}{J(2J-1)C_2(J)}$
${}^sQ_{22}(J)$	${}^sQ_{22}(J)$	$\frac{2[(J+1)Y-2J]^2}{(J+1)C_2(J)}$
${}^sR_{22}(J)$	${}^oP_{22}(J+1)$	$\frac{2J(J+2)Y^2}{(2J+3)C_2(J)}$

TABLE 1 (continued)

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${}^1X \rightarrow {}^1D$	${}^3D \rightarrow {}^3F$	1-factors
${}^1P_{11}(J)$	${}^3R_{11}(J-1)$	$\frac{(J^2-1)[(J+1)u_2+(Y-2)-2J(J+2)]^2}{(2J-1)C_2(J)}$
${}^1Q_{11}(J)$	${}^3Q_{11}(J)$	$\frac{[(J^2+J-1)u_2-(Y-2)-2J^2(J+2)]^2}{J C_2(J)}$
${}^1R_{11}(J)$	${}^3P_{11}(J+1)$	$\frac{J(J+2)^2[J u_2-(Y-2)-2J(J+1)]^2}{(J+1)(2J+3)C_2(J)}$
${}^1P_{21}(J)$	${}^3R_{21}(J-1)$	$\frac{(J^2-1)[u_2+(J+1)(Y-2)]^2}{J C_2(J)}$
${}^1Q_{21}(J)$	${}^3Q_{21}(J)$	$\frac{(2J+1)[(J^2+J-1)(Y-2)-u_2]^2}{J(J+1)C_2(J)}$
${}^1R_{21}(J)$	${}^3P_{21}(J+1)$	$\frac{J(J+2)[J(Y-2)-u_2]^2}{(J+1)C_2(J)}$
$P_2(J)$	$R_2(J-1)$	$\frac{(J+1)[(J^2-1)u_2+(J-1)(Y-2)-2J^2(J+2)]^2}{J(2J-1)C_2(J)}$
$Q_2(J)$	$Q_2(J)$	$\frac{[(J^2+J-1)u_2-(Y-2)-2J(J+1)(J+2)]^2}{(J+1)C_2(J)}$
$R_2(J)$	$P_2(J+1)$	$\frac{J(J+2)[J u_2-(Y-2)+2J(J-2)]^2}{(2J+3)C_2(J)}$

TABLE 2

branches	1-factors		
	${}^3D(a) \rightarrow {}^3D(a)$	${}^3D(a) \rightarrow {}^3D(b)$	${}^3D(b) \rightarrow {}^3D(b)$
$P_1(J)$	J	$\frac{(J-1)J}{2(2J+1)}$	$\frac{(J-2)J(2J+1)}{(J-1)(2J-1)}$
$Q_1(J)$	0	0	$\frac{(J+1)(2J+1)}{J^2}$
${}^1R_1(J)$	$J+1$	$\frac{(J-1)(J+1)}{2(2J+1)}$	$\frac{(J-1)(J+1)(2J+3)}{J(2J-1)}$
${}^1P_{21}(J)$	0	$\frac{(J-1)^2(J+1)^2}{J^2(2J+1)}$	$\frac{2J-1}{(J-1)J^2}$
${}^1Q_{21}(J)$	0	$\frac{J-1}{J^2}$	$\frac{(J-1)(J+1)}{J^2}$
${}^1R_{21}(J)$	0	$\frac{(J-1)(J+2)}{2J+1}$	0
${}^3P_{11}(J)$	0	$\frac{(J-2)(J+1)(J+2)^2}{2J^2(2J+1)}$	$\frac{(J-1)(J+1)}{J^2(2J-1)(2J+1)}$
${}^3Q_{21}(J)$	0	$\frac{2(J+2)}{J^2}$	0
${}^3R_{21}(J)$	0	$\frac{(J-1)(J+2)(J+3)}{2J(2J+1)}$	0

TABLE 2 (continued)

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branches	1-factor		
	${}^1D(a) \rightarrow {}^1D(a)$	${}^1D(a) \rightarrow {}^1D(b)$	${}^1D(b) \rightarrow {}^1D(b)$
${}^0P_{11}(J)$	0	$\frac{J}{2}$	0
${}^1Q_{11}(J)$	0	0	$\frac{(J-1)(J+1)}{J^2}$
${}^0R_{11}(J)$	0	$\frac{J+1}{2}$	$\frac{2J+3}{J(J+1)^2}$
$P_1(J)$	$\frac{(J-1)(J+1)}{J}$	$\frac{J-1}{J^2}$	$\frac{(J-1)^2(J+1)^2}{J^2}$
$Q_1(J)$	$\frac{2J+1}{J(J+1)}$	$\frac{2J+1}{J^2(J+1)^2}$	$\frac{(2J+1)(J^2+J-1)^2}{J^2(J+1)^2}$
$R_1(J)$	$\frac{J(J+2)}{J-1}$	$\frac{J+2}{(J+1)^2}$	$\frac{J^2(J+2)^2}{(J+1)^2}$
${}^0P_{21}(J)$	0	$\frac{(J-2)(J-1)(J+2)^2}{2J^2(J+1)}$	$\frac{2J-1}{J^2(J+1)}$
${}^1Q_{21}(J)$	0	$\frac{2(J-1)(J+2)(2J+1)}{J^2(J+1)^2}$	$\frac{J(J+2)}{(J+1)^2}$
${}^0R_{21}(J)$	0	$\frac{(J-1)^2(J+2)(J+3)}{2J(J+1)^2}$	0
${}^1P_{12}(J)$	0	$\frac{J(J+2)}{2(2J+1)}$	0
${}^0Q_{12}(J)$	0	0	0
${}^1R_{12}(J)$	0	$\frac{(J+1)(J+2)}{2(2J+1)}$	$\frac{J(J+2)}{(J+1)^2(2J+1)(2J+3)}$
${}^0P_{22}(J)$	0	$\frac{(J-1)(J+2)}{2J+1}$	0
${}^1Q_{22}(J)$	0	$\frac{J+2}{(J+1)^2}$	$\frac{J(J+2)}{(J+1)^2}$
${}^0R_{22}(J)$	0	$\frac{J^2(J+2)^2}{(J+1)^2(2J+1)}$	$\frac{2J+1}{(J+1)^2(J+2)}$
$P_2(J)$	$\frac{(J-2)(J+2)}{J}$	$\frac{(J-2)(J-1)(J+2)}{(J+1)(2J+1)}$	$\frac{J(J+2)(2J-1)}{(J+1)(2J+1)}$
$Q_2(J)$	$\frac{4(2J+1)}{J(J+1)}$	$\frac{2(J-1)}{(J+1)^2}$	$\frac{J(2J+1)}{(J+1)^2}$
$R_2(J)$	$\frac{(J-1)(J+3)}{J-1}$	$\frac{(J-1)^2J(J+3)}{2(J+1)^2(2J+1)}$	$\frac{(J+1)(J+3)(2J+1)}{(J+2)(2J+3)}$

In order to be able to also calculate the intensity distribution for $^3\Pi \rightarrow ^3\Pi$, we will give the elements of $S(^3\Pi)$. These are the following:

$$\left. \begin{aligned} S_{11} &= \frac{\sqrt{J(J+1)}[u_1 + (Y-2)]}{2\sqrt{C_1(J)}}, & S_{12} &= -\frac{\sqrt{2(J^2-1)}}{\sqrt{C_1(J)}}, & S_{13} &= \frac{\sqrt{(J-1)(J+2)}[u_1 - (Y-2)]}{2\sqrt{C_1(J)}}, \\ S_{21} &= \frac{\sqrt{2J(J+1)}}{\sqrt{C_2(J)}}, & S_{22} &= \frac{Y-2}{\sqrt{C_2(J)}}, & S_{23} &= -\frac{\sqrt{2(J-1)(J+2)}}{\sqrt{C_2(J)}}, \\ S_{31} &= \frac{\sqrt{J(J+1)}[u_1 - (Y-2)]}{2\sqrt{C_3(J)}}, & S_{32} &= \frac{\sqrt{2J(J+2)}}{\sqrt{C_3(J)}}, & S_{33} &= \frac{\sqrt{(J-1)(J+2)}[u_1 + (Y-2)]}{2\sqrt{C_3(J)}} \end{aligned} \right\} \quad (6)$$

where the first indices 1,2,3 refer to the states $K = J-1, J, J+1$, and the second 1,2,3 refer to $\Omega = 0,1,2$. The amplitudes q_a can be taken from Table 2. The phases of all of the elements of q_a could, for example, be taken to be positive and real*. The formulas for the intensities in the general case can now be given as

$$\begin{aligned} q_{ik}(J'; J'') &= S_{i1}(J', Y') q_{a11}(J'; J'') S_{k1}(J'', Y'') \\ &+ S_{i2}(J', Y') q_{a22}(J'; J'') S_{k2}(J'', Y'') \\ &+ S_{i3}(J', Y') q_{a33}(J'; J'') S_{k3}(J'', Y'') \quad (i, k = 1, 2, 3), \end{aligned} \quad (7)$$

where J', Y' refer to the initial state and J'', Y'' refer to the final state. The formulas for the limiting cases $^3\Pi(a) \rightarrow ^3\Pi(a)$, $^3\Pi(a) \rightarrow ^3\Pi(b)$, $^3\Pi(b) \rightarrow ^3\Pi(b)$ are contained in Table 2, where the $^3\Pi$ terms are assumed to be normal**.

One does not have to give the explicit intensity formulas as in the general case because experience shows that for most of the $^3\Pi \rightarrow ^3\Pi$ bands, the parameters Y', Y'' of the second terms differ

* See Hill and van Vleck, l.c. pg. 265.

** In the case a, the values $\Omega=0,1,2$ correspond to $K=J-1, J, J+1$ for normal terms (i.e., the indices 1,2,3). For reverse terms, on the other hand, this corresponds to $K=J+1, J, J-1$ (i.e., the indices 3,2,1). Thus, for example, the expressions given in Table 2 under RP_{31} are to be given the name $^3P_{31}, P_{11}, ^3P_{11}$ for reverse terms.

only slightly*. Then the conditions are easily overseen. From the fact that $q_{a,11}(J-1;J), q_{a,22}(J-1;J), q_{a,33}(J-1;J)$ are equal among themselves and that $q_{a,11}(J+1;J), q_{a,22}(J+1;J), q_{a,33}(J+1;J)$ are almost equal, and also because $3S=1$ the expressions

$$S_{i1}(J', Y') S_{k1}(J'', Y'') + S_{i2}(J', Y') S_{k2}(J'', Y'') + S_{i3}(J', Y') S_{k3}(J'', Y'')$$

for $i = k$ are close to 1, and for $i \neq k$ are close to 0 and it follows that only the main branches P_1, P_2, P_3 and R_1, R_2, R_3 are present with measurable intensity. The Q branches are found to be much weaker than these which immediately follow by comparing $q_{a,11}(J;J)$ and $q_{a,11}(J \pm 1;J)$. /585

Table 3 gives the expressions for the intercombination bands $^1\Sigma \longleftrightarrow ^3\Pi$. They contain the formulas derived by Schlapp [5] as special cases. Here λ is a real constant (λ corresponds to E/D in the case of Schlapp).

Comparison with experience. Quantitative intensity measurements in triplet bands were recently published by Nolan and Jenkins [6]. They measured intensities of the lines of the $^3\Pi \rightarrow ^3\Sigma, 0-0$ band of PH. From their measurements, after having determined the emission temperature, they plotted the values of the (experimental) i-factors as a function of the rotation quantum number J. We can /586 calculate the theoretical i-factors according to our Table 1. The constant Y for the $^3\Pi$ -Term term of PH is $Y = -14.4$ [6]. From Figures 1a and 1b it can be seen, the upper part of which represents the experimental results and the lower part of which contains the curves calculated according to Table 1** that the agreement is very good.

* For example, in the case of the $C^3\Pi \rightarrow N^3\Pi, 0-0$ band of TiO, $Y' = 180, Y'' = 188$. For the $C^3\Pi \rightarrow B^3\Pi, 0-0$ of N_2 , $Y' = 21.5, Y'' = 25.9$. For the $B^3\Pi \rightarrow A^3\Pi, 0-0$ band of C_2 we have $Y' = -9.4, Y'' = -10.4$. see for example, A. Budo, ZS. for Phys. 98, 437, 1936.

** The proportionality constant with the curves was selected so that the measured and calculated values of Q_1 agree as well as possible.

TABLE 3

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$1\Sigma \rightarrow 3\Pi$	$3\Pi \rightarrow 1\Sigma$	1-factors
$Q_P(J)$	$Q_R(J-1)$	$\frac{(J+1)[J(u_1+Y-2)-2\lambda(J-1)]^2}{C_1(J)}$
$R_Q(J)$	$P_Q(J)$	$\frac{4\lambda^2(J-1)^2(J+1)^2(2J+1)}{C_1(J)}$
$S_R(J)$	$Q_P(J-1)$	$\frac{J(J+1)^2[(u_1+Y-2)-2\lambda(J-1)]^2}{C_1(J)}$
$P(J)$	$R(J-1)$	$\frac{2(J+1)[2J+\lambda(Y-2)]^2}{C_2(J)}$
$Q(J)$	$Q(J)$	$\frac{2\lambda^2(2J+1)(Y-2)^2}{C_2(J)}$
$R(J)$	$P(J+1)$	$\frac{2J[2(J+1)+\lambda(Y-2)]^2}{C_2(J)}$
$Q_P(J)$	$S_R(J-1)$	$\frac{J^2(J+1)[(u_1-Y+2)+2\lambda(J+2)]^2}{C_3(J)}$
$P_Q(J)$	$R_Q(J)$	$\frac{4\lambda^2J^2(J+2)^2(2J+1)}{C_3(J)}$
$Q_R(J)$	$Q_P(J+1)$	$\frac{J[(J+1)(u_1-Y+2)+2\lambda J(J+2)]^2}{C_3(J)}$

This is especially true if one considers the fact that several lines coincide in the spectrum and that the 1-factors are not directly measured quantities. This also includes the inaccuracy of the temperature determination.

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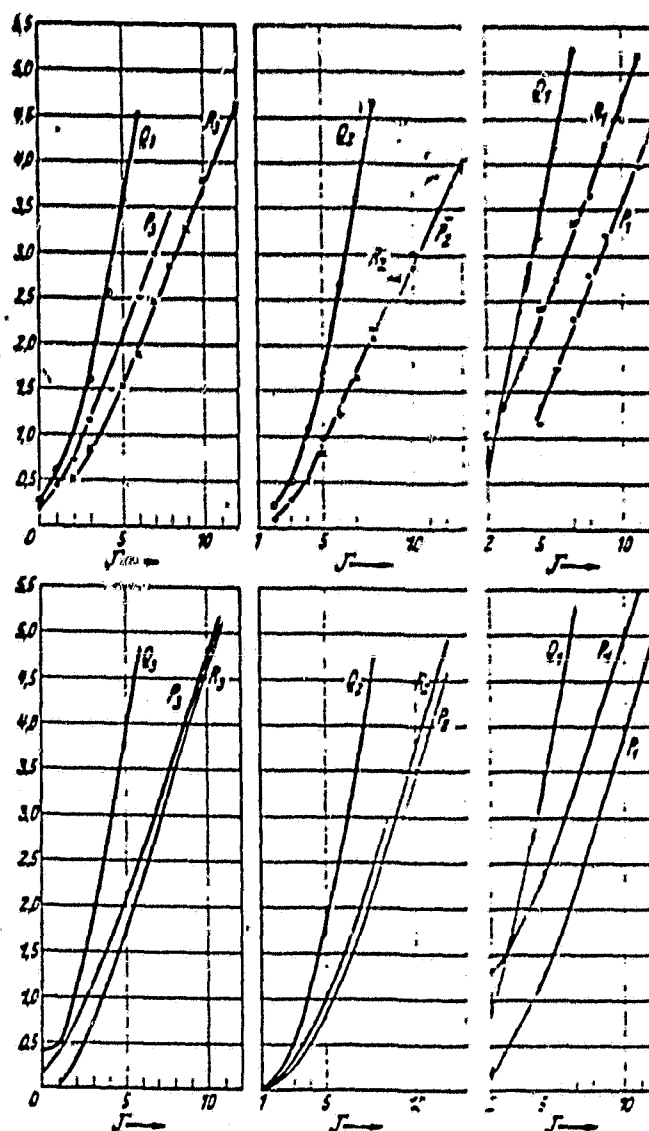


Figure 1a

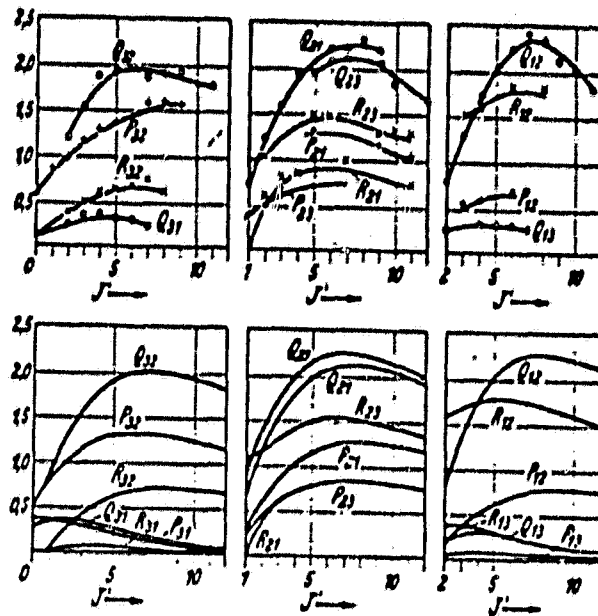


Figure 1b

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